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Photochemical oxidation of phenolic wastewaters and its kinetic study

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ABSTRACT

The present work was carried out to study the photochemical oxidation of phenol and *p*-chlorophenol in a batch recycle photochemical reactor using ultraviolet irradiation, hydrogen peroxide and TiO_2 (as photocatalyst). The study revealed that the combined treatment process was the most effective process under acidic conditions and showed a higher rate of degradation of phenol and *p*-chlorophenol at a very short radiation time. The reaction was found to follow the first order kinetics and was influenced by the pH, the input concentration of H_2O_2 and the dosing amount of the TiO_2 photocatalyst. The experimental results showed that the maximum % degradation were obtained at a pH value of 4, with H_2O_2 concentration ranging from 200 to 550 ml l^{-1}, and TiO_2 dosing ranging from 1.0 to 2.5 g l^{-1} for UV/H_2O_2/TiO_2 combined system under bubbling of air. The results indicate maximum (74.6% and 79.8%) degradation of phenol and *p*-chlorophenol respectively within 90 min of radiation time. The work also covered the few other aspects related to the advanced oxidation processes such as chemical oxygen demand (COD) analysis, energy consumption and dechlorination efficiency.

Keywords: Advanced oxidation; Photochemical oxidation; Degradation; First-order kinetics; *p*-Chlorophenol; UV/H_2O_2/TiO_2 system; phenol

1. Introduction

Environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants. Ever increase in living standards led to setting up of various processing plants which contributes remarkably to the wastewater volumes. Most conventional treatment processes are effective in water treatment but they only transfer the contaminants from one medium to another or generate waste that requires further treatment and disposal [1,2]. There is a need to develop effective methods for degradation of resistant pollutants to less harmful compounds or for their complete mineralization. The transfer of contaminants from water to another phase is not an ideal remedy. Destructive oxidation treatments provide more permanent solutions [3]. The focus on waste minimization and water conservation in the recent years resulted in the discovery of various treatment processes, one of them being advanced oxidation processes (AOP). These refer to the chemical treatment processes which follow oxidation route and are particularly employed to degrade biologically toxic and non degradable chemicals [4]. Photocatalytic degradation oxidizes harmful environment pollutants and converts it into harmless innocuous substances.

Many processes such as chemical oxidation, Fenton and photo-Fenton processes, ultraviolet (UV) based

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processes, photocatalytic redox processes, supercritical water oxidation, sonolysis, and electron beams and γ-ray irradiation come under advanced oxidation techniques [4]. High energy requirement of photo oxidation with ozone and hydrogen peroxide is a major disadvantage when the organic or inorganic pollutants of wastewater strongly absorb UV-radiation. Waste disposal is a major issue in photo-Fenton process due to the production of inorganic sludge [5].

The efficacy of photochemical process depends strongly on the rate of generation of the free radicals along with the extent of contact of the generated radicals with the contaminant molecules. Photocatalysis, using ultraviolet light and titanium dioxide catalyst has emerged out to be a powerful source of hydroxyl radical generation. Although many catalysts have been brought into use but TiO_2 is found to be a promising photocatalyst due to its low cost, higher stability, non-toxicity and efficient performance [6].

Phenol and *p*-chlorophenol are put up under priority pollutants by U.S.EPA due to their high toxicity, carcinogenicity, and persistence [7,8] and hence required to be degraded. There are number of articles available on the oxidation of phenol and *p*-chlorophenol using UV/H_2O_2, photo-Fenton process or photocatalysis [9–14], but few have studied the oxidation of phenol and *p*-chlorophenol using UV/H_2O_2/TiO_2 combined system and that too at lower pollutant concentration.

In recent years the combinations of solar irradiation and TiO_2/H_2O_2 have been used to enhance the biodegradability of phenolic wastewater [15]. Hussain et al. evaluated the effect of the ratio of food to microorganism (F/M) and nature of sludge on methanogenesis of phenol in the batch reactors [16]. They also treated phenolic wastewater in upflow anaerobic sludge blanket (UASB) reactor with varying amount of phosphorous [17].

In this study, photocatalytic degradation rates of phenol and *p*-chlorophenol have been examined in the presence of TiO_2 and/or H_2O_2 under UV illumination. Effects of the pH, concentration of H_2O_2 and the dosing amount of the TiO_2 photocatalyst on degradation rate were also evaluated. Kinetic study was also performed varying operating conditions of the system. Finally a comparison of energy consumption of different process combinations was also estimated.

2. Materials and methods

Phenol and *p*-chlorophenol were purchased from Merck, India. Hydrogen peroxide solution (30% w/v) in stable form was purchased from Finar Reagents. Photocatalyst (TiO_2, AR grade) and all other chemicals obtained were of analytical reagent grade quality and were used as received. Solutions were prepared using doubly distilled, deionized water.

2.1. Experimental setup

All experiments were performed in a batch reactor. The reactor was cylindrical with 250 ml volume and was made from quartz glass which was available for the transfer of the radiation. Irradiation was achieved by using UV lamp of 125 W (medium pressure lamp) which was immersed in the glass tube. The UV lamp was equipped with a cooling water space which was placed in the reactor vessel. The reaction chamber was filled with the reaction mixture, which was placed between the reactor walls and UV lamp system. Mixing was accomplished using air bubbler to keep the photocatalyst in suspension.

2.2. Photo-degradation process

For each experiment, synthetic aqueous solution of 50–200 mg l^{-1} phenol and *p*-chlorophenol was prepared separately in ultrapure deionized water. The laboratory unit was filled with 100 ml of the solution. For runs using UV/H_2O_2 system, hydrogen peroxide at different volumes was injected in the reactor before the beginning of each run and for runs using UV/TiO_2 system, TiO_2 in different amounts were used into the solution before the beginning of each run. The pH value of the solution was adjusted by the addition of HCl and NaOH solution. The suspended TiO_2 solution was mixed well using stirrer for 30 min so that adsorption equilibrium was reached. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment and it irradiated upto 90 min for all experiments. Air was bubbled into the solution throughout the experiment to keep the photocatalyst in suspension and also as a source of oxygen for effective degradation.

2.3. Analytical methods

Samples were taken at every 15 min time interval from the reaction vessel and pipetted into test tubes. The samples were immediately analyzed to avoid further reaction. Concentration changes of phenol and *p*-chlorophenol were determined by UV-vis spectrophotometer (APHA, 2005). Samples at different time intervals were also analyzed to determine dechlorination efficiencies (APHA, 2005). COD analysis was carried out via a DR 5000 spectrophotometer (HACH Co., USA) as per APHA (2005) [18]. Hexachlorobenzene is usually extracted from water with organic solvents for analysis (EPA 1988e, 1988f; Munch et al. 1990). For analysis of intermediate compounds GC-MS was used. Phenol, *p*-chlorophenol and other intermediates were extracted by organic solvent and concentrated by adsorption on adsorbent cartridges or disks. After subsequent solvent desorption, it was analysed by fused silica capillary column (Rxi®-5ms Columns).

3. Results and discussion

The effect of pH was evaluated by taking a random amount of oxidant (H_2O_2 = 75 ml l^{-1}) and photocatalyst (TiO_2 = 0.5g l^{-1}) and substrate concentration of 50 mg l^{-1}. After 90 min of irradiation the samples were analyzed and the percent degradation was found to be 68.2%, 50.7% and 39.1% for phenol at pH 4, 7 and 9 respectively and 70.4%, 55.7% and 42.3% for *p*-chlorophenol at pH 4, 7 and 9 respectively. The results revealed a maximum efficiency at acidic pH. This may be because of acidic pH makes the photocatalyst surface positively charged hence attracts the pollutant molecule leading to greater adsorption and hence higher degradation rate. At basic pH, the photocatalyst surface becomes negatively charged and hence low degradation rate. So keeping feed solution pH 4, the optimum amounts of oxidant and photocatalyst was determined.

3.1. Direct photolysis (only UV)

In this system, the reactor was loaded with solution and was irradiated by ultra violet lamp. The degradation in this system took place at a very slow rate. When the solution is radiated by the ultra violet lamp, the degradation takes place via formation of hydroxyl radicals.

3.2. UV/H_2O_2 process

Hydrogen peroxide is a very efficient oxidant. The degradation in this system takes place via the formation of hydroxyl radicals [5] which are formed as per Eq. (1):

$$H_2O_2 + h\nu \rightarrow 2OH \tag{1}$$

The hydroxyl radicals formed attack the pollutant, thereby degrading it. The combination of ultraviolet rays and oxidant efficiently degrades the phenolic compounds in wastewaters.

3.2.1. Effect of initial H_2O_2 concentration

Oxidant concentration greatly influences the rate of photocatalytic oxidation. To evaluate this effect, experiments were performed at different concentrations of H_2O_2 maintaining acidic feed phase (pH at 4.0) and a fixed concentration of pollutants. The H_2O_2 concentration was varied from 100 to 550 ml l^{-1} and the pollutant concentration from 50 to 200 mg l^{-1} for both phenol and *p*-chlorophenol. The results indicated the effect of H_2O_2 concentration on degradation efficiency of UV/H_2O_2 process. For both phenol and *p*-chlorophenol, with the increase in H_2O_2 concentration from 200 to 550 ml l^{-1}, the percent degradation increased. Further increase in H_2O_2 concentration lowered the degradation rate. This is because of the excess H_2O_2 reacts with the hydroxyl radicals earlier formed and hence acts as an inhibiting agent of degradation by consuming the hydroxyl radicals responsible for degrading the pollutant molecule [5]. Excess Hydrogen peroxide reacts with hydroxyl radicals as per Eq. (2):

$$H_2O_2 + 2OH^{\bullet} \rightarrow H_2O + 3/2O_2 + H_2 \tag{2}$$

when concentration of H_2O_2 is above 550 ml l^{-1}, its hydroxyl radical scavenging effect becomes predominant [19]. The UV/H_2O_2 system indicated a higher degradation as compared to only UV process for both phenol and *p*-chlorophenol.

3.3. UV/TiO_2 process

The presence of catalyst in a reaction system enhances the rate of reaction considerably. When the photocatalyst TiO_2 is irradiated using ultraviolet rays, the reaction takes place as per given by Eqs. (3) and (4):

$$TiO_2 + h\nu \rightarrow e^{-}_{CB} + h^{+}_{VB} \tag{3}$$

$$TiO_2\left(h^{+}\right) + H_2O \rightarrow \left(OH^{\bullet}\right) + H^{+} \tag{4}$$

The amount of catalyst affects the reaction rate by providing the surface for the adsorption as well as generating oxidative valence band holes and electrons. The powerful hydroxyl radicals generated by the process successfully degrades the pollutant molecule in wastewaters.

3.3.1. Effect of dosing amount of TiO_2 photocatalyst

To determine the effect of catalyst loading on the reaction rate, several experiments were conducted at catalyst loading from 1.0 to 2.5 g l^{-1} (feed phase pH at 4) and pollutant concentration from 50 to 200 mg l^{-1} for both phenol and *p*-chlorophenol.

The observation clearly indicated that the increase in amount of catalyst loading upto 2.5 g l^{-1}, the rate of degradation increased. The increase in degradation rate may be explained by the fragmentation of catalyst which produces higher surface area. Thereafter with further increase in catalyst loading the degradation rate starts declining. This nature is due to the screening effect, that is, above a certain amount of catalyst loading (2.5 g l^{-1}), the turbidity of the solution increases and ultraviolet rays start getting scattered, hence reducing the optical path [19].

The presence of photocatalyst, TiO_2 in this system increased the rate of degradation of both phenol and *p*-chlorophenol. This system showed higher percent degradation in comparison to the only UV and UV/H_2O_2 process.

3.4. UV/H_2O_2/TiO_2 process

In this system, keeping H_2O_2 concentration at 550 ml l^{-1} and TiO_2 loading at 2.5 g l^{-1}, feed solution of 50–200 mg l^{-1} phenol and *p*-chlorophenol, was irradiated under ultraviolet rays. As expected, ultraviolet rays coupled with oxidant (H_2O_2) and photocatalyst (TiO_2) accelerated the rate of degradation remarkably. The highest removal was observed in UV/TiO_2/H_2O_2 system compared to UV, UV/H_2O_2 and UV/TiO_2 systems which were mainly attributed due to TiO_2-catalysed decomposition of H_2O_2 to form more active free radicals.

3.4.1. Active radical formation mechanism in UV/H_2O_2/TiO_2 process

When the reaction mixture is irradiated by ultraviolet rays, hydroxyl radicals are produced which further react in the solution to degrade the pollutant. The formation of active radical takes place as per Eqs. (5)–(11):

$$H_2O + h\nu \rightarrow OH^{\bullet} + H^+ \qquad (5)$$

$$H^{\bullet} + O_2 \rightarrow HO^{\bullet}_2 \qquad (6)$$

$$TiO_2 + h\nu \rightarrow e^-{}_{CB} + h^+{}_{VB} \qquad (7)$$

$$TiO_2(e^-) + O_2 \rightarrow O^{\bullet}_2 \qquad (8)$$

$$TiO_2(h^+) + H_2O \rightarrow OH^{\bullet} + H^+ \qquad (9)$$

$$H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^- \qquad (10)$$

$$OH^- + h^+ \rightarrow OH \qquad (11)$$

The samples from photochemical reactor were analyzed at every 15 min to study the effect. Few results are listed in Table 1. It can be deduced from the results that the maximum degradation is still observed at pH 4. This is because at higher pH, H_2O_2 decomposes into oxygen and water [20]. This lowers the quantity of hydroxyl radicals resulting into decreased degradation rate.

Table 1
Effect of pH on percent degradation of phenol and *p*-chlorophenol at initial concentrations 50–200 mg l^{-1} in UV/H_2O_2/TiO_2 process

Pollutant	Process	pH	Concentration (mg l^{-1})	Percent degradation		
				30 min	60 min	90 min
Phenol	UV/H_2O_2/TiO_2	4	50	19.8	42.4	74.6
			100	13.7	43.8	70.1
			150	14.6	46.2	71.7
			200	14.9	38.2	67.5
		7	50	10.6	29.4	55.6
			100	11.3	32.7	50.9
			150	12.4	48.4	52.9
			200	10.7	24.1	49.7
		9	50	7.8	25.8	43.8
			100	12.8	27.9	39.6
			150	9.1	26.2	43.3
			200	8.7	21.8	39.8
p-Chlorophenol	UV/H_2O_2/TiO_2	4	50	19.6	49.6	79.8
			100	19.9	47.9	77.1
			150	17.7	41.9	72.7
			200	15.7	38	69.9
		7	50	15.8	35.2	62.4
			100	9.6	27.4	58.6
			150	11.9	29.5	54.5
			200	9.5	25.7	52.4
		9	50	11.8	28.6	49.6
			100	5.3	18.4	47.7
			150	7.4	21.9	46.2
			200	7.2	29.2	45.6

Figs. 1 and 2 indicate the comparison between different processes for phenol and *p*-chlorophenol degradation. It is clear by the given figures that amongst the different processes used, the combined treatment process ($UV/H_2O_2/TiO_2$) showed the highest percent degradation in case of both phenol and *p*-chlorophenol as compared to the other systems used. The effect of substrate concentration can also be judged by Figs. 1 and 2. As the substrate concentration increases, the percent degradation decreases. This might be because the initial substrate concentration is increased but reaction time is kept constant, that is 90 min and lower efficiency is also caused by light absorption (by the substrate), which decreases the incidence of radiation on the TiO_2 surface so that decreasing the photocatalysis efficiency and hence a maximum of 74.6% and 79.8% degradation is observed at initial substrate concentration of 50 mg l^{-1} for the combined $UV/H_2O_2/TiO_2$ process.

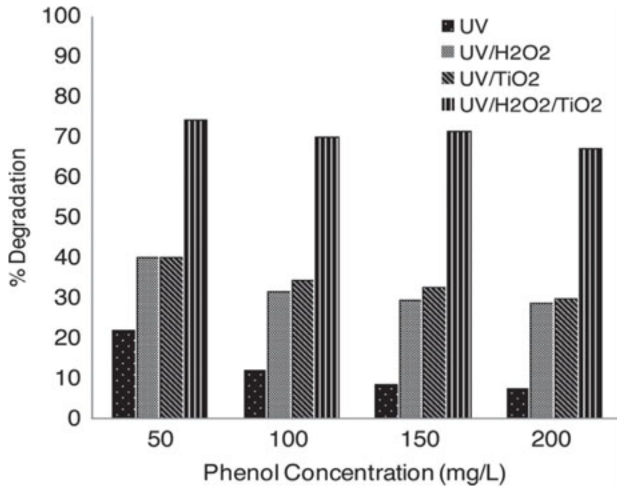

Fig. 1. Comparison between different processes for phenol degradation.

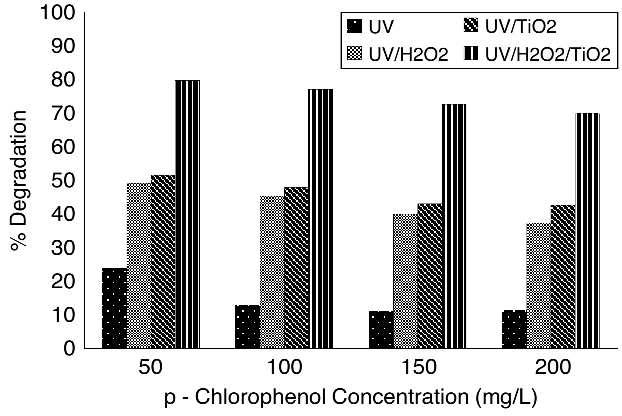

Fig. 2. Comparison between different processes for *p*-cholorophenol degradation.

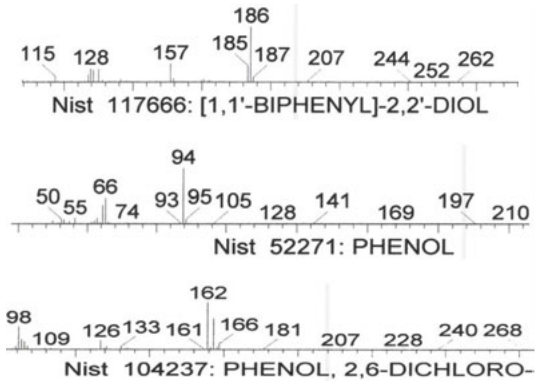

Fig. 3. GC-MS spectrum of biphenyl diol, phenol and 2,6 dicholrophenol.

3.5. COD analysis

COD analysis was carried out with samples at different time interval. It was observed that the COD removal efficiency was very low (25–30%) for all these degradation processes, which might be because of only partial oxidation of the pollutants. Samples were analysed by GC-MS and it was found that phenol degradation takes place via the formation of biphenyl diol (Mol. wt. 186) as an intermediate (Fig. 3). On the other hand phenol and 2,6 dicholorophenol (Fig. 3) are formed as intermediates of *p*-chlorophenol. The similar phenomenon was observed by Essam et al. for photochemical–biological degradation of *p*-chlorophenol, wherein the lower COD removal was observed due to the presence of hydroquinone and catechol as intermediates in the irradiated samples [7].

4. Degradation rate kinetics

The kinetics study of photodegradation of phenol and *p*-chlorophenol was investigated for UV, UV/H_2O_2, UV/TiO_2 and $UV/H_2O_2/TiO_2$ systems (Table 2). The loss

Table 2
Kinetics data for phenol and *p*-chlorophenol for different systems used

Pollutant	System used	k (min^{-1})	Half life ($t_{1/2}$, min)
Phenol	UV	0.0028	247.6
	UV/H_2O_2	0.0057	121.6
	UV/TiO_2	0.0059	117.5
	$UV/H_2O_2/TiO_2$	0.0143	48.5
p-Chlorophenol	UV	0.0031	223.6
	UV/H_2O_2	0.0076	91.2
	UV/TiO_2	0.0086	80.6
	$UV/H_2O_2/TiO_2$	0.0153	45.3

of total concentration of phenol and *p*-chlorophenol was observed as a function of irradiation time and data were fitted to a first-order rate model. Figs. 4 and 5 showed degradation kinetics for UV/H_2O_2/TiO_2 systems:

$$\ln\left(C_t/C_0\right) = -kt \qquad (12)$$

where C_0 and C_t are the concentration of pollutant at irradiation times 0 and t, k is the first-order rate constant (min^{-1}) and t is the irradiation time (min).
Half life time equation:

$$t_{1/2} = \ln\left(2\right)/k \qquad (13)$$

The individual rate constants and half life were determined using Eqs. (12) and (13) respectively. The results are listed in Table 2 which indicates maximum value of rate constant of 0.0143 and 0.0153 min^{-1} and minimum half life period of 48.5 and 45.3 min for phenol and *p*-chlorophenol respectively for the combined UV/H_2O_2/TiO_2 process.

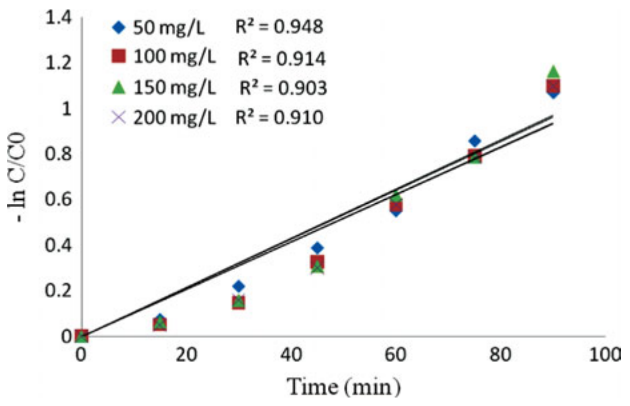

Fig. 4. Phenol degradation rate kinetics for UV/H_2O_2/TiO_2 process at concentrations 50–200 mg l^{-1}.

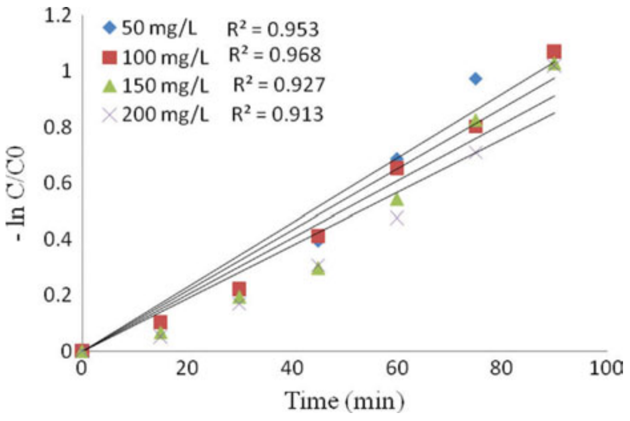

Fig. 5. *p*-Chorophenol degradation rate kinetics for UV/H_2O_2/TiO_2 process at concentrations 50–200 mg l^{-1}.

5. Reductive dechlorination

Reductive dechlorination is a term that is used to describe certain types of degradation of chlorinated organic compounds by chemical reduction with release of inorganic chloride ions. Generally, chlorinated compounds exhibit resistance to biodegradation, and chemical oxidation is usually employed to treat solutions of these compounds prior to biological process [21].

In order to study the phenomena of reductive dechlorination, chloride ion generation was studied with samples at different time interval from photochemical reactor (combined UV/H_2O_2/TiO_2 process), which showed the concentration of the free chloride produced during the oxidation of *p*-chlorophenol and the results revealed the generation of maximum 44.8 mg l^{-1} chloride ions (80% degradation *p*-chlorophenol) of at the end of 90 min of irradiation time for 200 mg l^{-1} initial concentration of *p*-chlorophenol.

6. Energy consumption

For any system to be considered for practical applications, an estimation of energy consumption by the system is a must factor which should be evaluated. Energy consumption in real sense defines the system's efficiency. The energy consumption was calculated using Eq. (14):

$$\text{Daily consumption (kWh)} = \text{Wattage} \times \text{hours used per day}/1000 \qquad (14)$$

The evaluation of energy consumption was calculated for 100% degradation by each system. Time taken by each system for 100% degradation was calculated and substituted in Eq. (14) for the evaluation of power consumption. Fig. 6 indicates the energy consumption comparison between different systems used. It was observed

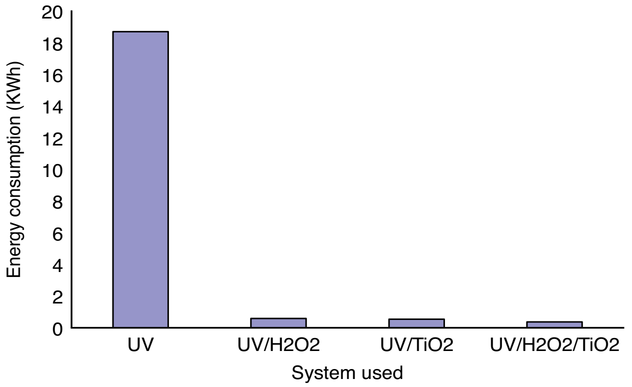

Fig. 6. Energy consumption by different processes at optimum condition.

that the highest amount of energy was consumed by UV system as compared to UV/H_2O_2, UV/TiO_2 and UV/H_2O_2/TiO_2 systems for same irradiation time which is due the production of good amount of hydroxyl radicals hence higher removal in less irradiation time and lower power consumption.

7. Conclusions

This study showed the potentialities of photocatalytic degradation in water purification. Out of different processes employed, a significant enhancement of the photocatalytic activity was observed in the system using combination of oxidant and photocatalyst irradiation under UV light. Concentration of both oxidant and photocatalyst greatly influences the degradation rate. Also the process was observed to be strongly pH dependent. The degradation follows first order kinetics. Photodegradation can be a recommended approach for the treatment of phenolic wastewaters. Keeping in view all the factors, it can be easily said that the UV/H_2O_2/TiO_2 combined system is an efficient one amongst all other processes.

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